STUDIES IN GLASS SYSTEMS—MAGNETIC SUSCEPTIBILITY OF POLAR CRYSTALS DISSOLVED IN BORAX GLASS

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ABSTRACT. The present paper is an extension of the work done on magnetic properties of polar salts dissolved in glass (Majumdar and Saha, 1945) using a magnetic torsion balance instead of the Guoy balance. Alkali salts like NaCl, Li_2SO_4, Na_2SO_4 and K_2SO_4 were dissolved in fused borax and the diamagnetic susceptibilities of the dissolved salts determined. The values thus obtained are remarkably large, indicating an expansion of the lattice. This conclusion runs counter to that drawn from previous measurements of mole-refraction and Xray diffraction.

INTRODUCTION

The problem, in what form polar crystals exist when dissolved in a glass medium, has been engaging the attention of some workers during the last few years. Measurement of mole-refraction of various salts dissolved in fused boric oxide and borax glasses have brought out the fact that these salts are very strongly deformed in solid solution in glass, as shown by their remarkably small values of mole-refraction and the results in the main support the Deformation Rule proposed by Fajans (Majumdar and Sarma, 1942 ; Majumdar and Banerjee, 1946). In a previous paper (Majumdar and Saha 1945), the results of magnetic susceptibility of alkali chlorides dissolved in borax glass, as measured in a Guoy balance, were recorded. As is wellknown the sources of error in a Guoy balance are far too many and it is for this reason a more accurate method has been employed in this investigation. The magnetic torsion balance, first used by Krishnan and Banerjee, (1933) and later modified by Datta (1944), has been used to measure the diamagnetic susceptibility of the following glass systems :

$NaCl-Na_2B_4O_7$; $Li_2SO_4-Na_2B_4O_7$; $Na_2SO_4-Na_2B_4O_7$ and $K_2SO_4-Na_2B_4O_7$.

The salt-content of the glasses was determined analytically and their diamagnetic susceptibilities were determined from the additivity formula :

$$100\chi_g = p.\chi_1 + (100-p)\chi_2,$$

where χ_g represents the mass susceptibility of the glass (experimental value), χ_1, the mass susceptibility of the dissolved salt, χ_2, the mass susceptibility of borax, p, the percentage of the dissolved salt and (100-p) that of borax in the glass.

Preparation of the samples.—Lithium sulphate was prepared by dissolving lithium carbonate in dilute sulphuric acid and twice recrystallising in vacuum. Merck's *Pro Analyse* quality of NaCl, Na_2SO_4 and K_2SO_4 were recrystallised once from conductivity water and dried. Pure borax (Merck) was similarly recrystallised from its solution in conductivity water and the salts carefully dehydrated first in an air oven and then in a vacuum desiccator. The samples were prepared by fusion in a platinum crucible as described in the previous papers.

Analysis of the samples.—For the $NaCl-Na_2B_4O_7$ system, the chlorine content was determined by the following method. Weighed amounts of the glass were dissolved in hot water, acidified with nitric acid and excess of a standard solution of silver nitrate added. The whole solution was diluted to a definite volume (250 c.c.); 50 c.c. was dry-filtered and titrated against standard NH_4CNS solution, using ferric alum as indicator.

The total sodium was determined by taking a known weight of the glass in a weighed platinum crucible, treating it repeatedly with a mixture of HF and H_2SO_4 and evaporating to dryness until a constant weight was obtained. The sodium, corresponding to NaCl, was subtracted from this and the remainder agreed fairly well with the $Na_2B_4O_7$ of the glass.

For the sulphate glasses, the following procedure was adopted. Weighed amounts were dissolved in hot water, excess of HCl was added and the sulphate precipitated as $BaSO_4$ from the boiling solutions. The precipitation was carried out by taking the necessery precautions and the precipitated $BaSO_4$ weighed.

Determination of the Magnetic Susceptibility of the glass.—The magnetic susceptibility of the glass pieces was determined in a magnetic torsion balance after suspending them in two suitable liquids of known susceptibilities between the flat pole pieces of a powerful electro-magnet. The experimental piece was rigidly attached to one end of a vertical Pyrex glass rod about 15 cm. long, by slightly melting the borax glass at one point, the other end of the glass rod being attached to the middle of a fine silver wire stretched horizontally between a torsion head and a metal chuck. A small lateral displacement could thus be given by turning the torsion head. The whole thing was so adjusted that the glass piece was roughly at a distance of 3-4 cm. away from the edges of the flat pole pieces of the electro-magnet and was, therefore, in a non-homogeneous field with the gradient in the horizontal direction.

The glass piece was first suspended in a liquid of known susceptibility and the current switched on. The glass being dia-magnetic was displaced laterally along the gradient in a direction away from the field. The reflected light from a mirror on the glass rod very near the experimental piece was viewed through a tele-microscope and the torsion head turned until it came back to the original position.

If K_c be the volume susceptibility of the glass piece and K_1 that of the liquid, the force turning the piece from the field is given by

$$\tfrac{1}{2}A.\,H_x.\,\frac{dH_x}{dx}\,(K_c-K_1),$$

where A is the cross-section of the piece, H, the field strength, the x-direction being the horizontal one. If θ_1 is the angle through which the torsion head is turned, then this force is $R\theta_1$, where R is the torsional constant of the wire. Hence

$$\tfrac{1}{2}A.H_x.\,\frac{dH_x}{dx}\,(K_c-K_1)=R.\,\theta_1 \qquad \ldots\ (1)$$

If θ_2 be the angle through which the torsion head is turned while immersed in the second liquid of volume susceptibility K_2, then

$$\tfrac{1}{2}.\,A.\,H_x,\,\frac{dH_x}{dx}\,(K_c-K_2)=R,\,\theta_2 \qquad \ldots\ (2)$$

Dividing (1) by (2)

$$\frac{K_c-K_1}{K_c-K_2}=\frac{\theta_1}{\theta_2} \qquad \ldots\ (3)$$

K_1, K_2, θ_1, θ_2 being known, K_c can be calculated from (3). The mass susceptibility was determined by multiplying K_c by the density of the sample.

The liquids selected for immersion were Kahlbaum's pure pyridine and Merck's diethylaniline freshly redistilled. The values of mass susceptibilities of these are respectively -0.623×10^{-6} and -0.78×10^{-6} and their respective densities are 0.982 and 0.934 at 25°c (the average temperature of the experiments). These values are taken from the International Critical Tables. Thus K_1 and K_2 work out respectively -0.612×10^{-6} and -0.78×10^{-6}. Wider apart the values of K_1 and K_2, the greater will be the divergence between θ_1 and θ_2 and therefore smaller the experimental error.

In order to test the accuracy of the method and the purity of the liquids, a check experiment was performed by taking a crystal of known magnetic susceptibility and suspending it successively in distilled water and the same two liquids as before.

The calculated values compare favourably with the values given in the International Critical Table.

Although both borax and alkali sulphate crystals are optically anisotropic (bi-axial), yet the glass was perfectly isotropic as proved under crossed Nicols in a polarisation microscope. This may be due to the random distribution of the molecules in the glass neutralising the mutual anisotropic effects. They, however, showed slight *magnetic anisotropy*.

The densities of the glass pieces were determined at the room temperature in a hydrostatic balance using nitro-benzene as the suspending liquid, and unspun silk fibre for suspending the glass. The density of the sample of nitro-benzene was determined at the room temperature by a specific gravity bottle.

EXPERIMENTAL RESULTS

In the following table, the readings of the torsion head are recorded in columns 3 and 4 ; column 5 gives the value of volume susceptibility K_c and the last column gives the values of mass susceptibility.

TABLE I

Magnetic susceptibility data.

Sample No	% salt in glass	θ_1 (mean)	θ_2 (mean)	$K_c \times 10^6$	Density	Mass susceptibility $\times 10^6$
NaCl—$Na_2B_4O_7$ system						
1.	8.97	84°	69°	—1.55	2.325	—0.6667
2.*	14.85	74°	60°	—1.50	2.282	—0.6573
3.	15.22	98°	81°	—1.58	2.269	—0.6965
4.	16.84	55°	46°	—1.636	2.249	—0.7276
5.	17.22	54°	46°	—1.746	2.303	—0.7580
Li_2SO_4—$Na_2B_4O_7$ system						
1.	7.02	65°	51°	—1.392	2.381	—0.5846
2.	9.55	95°	79°	—1.610	2.383	—0.6759
3.	11.50	71°	60°	—1.70	2.379	—0.7145
4.	12.98	79°	68°	—1.819	2.379	—0.7643
Na_2SO_4—$Na_2B_4O_7$ system						
1.	8.68	41°	33°	—1.473	2.377	—0.6195
2.	10.67	57°	47°	—1.570	2.382	—0.6591
3.	13.43	40°	34°	—1.732	2.374	—0.7292
4.	15.62	38°	33°	—1.888	2.436	—0.7752
5.	17.36	50°	44°	—2.012	2.377	—0.8455
6.	17.71	170°	150°	—2.040	2.382	—0.8563
K_2SO_4—$Na_2B_4O_7$ system						
1.	5.46	88°	67°	—1.320	2.366	—0.558
2.	8.64	77°	60°	—1.370	2.357	—0.581
3.	11.14	107°	85°	—1.430	2.356	—0.607
4.	15.38	123°	102°	—1.540	2.356	—0.654
5.	18.42	92°	79°	—1.800	2.374	—0.758
$Na_2B_4O_7$—glass						
1.	0	73.5°	63.3°	—1.264	2.333	—0.5418
2.	0	100°	75°	—1.284	2.372	—0.5414

The following table records the values of mass susceptibility and gm.-molecular susceptibilities of the dissolved salts calculated from the additivity

formula, taking the observed values of the susceptibilities of the glass pieces ; the value for borax glass which is supposed to remain unaltered is taken as -0.5416×10^{-6}, the mean of the two observed values. These values are compared with those of the pure salts.

TABLE II

Mass and gm.-molecular susceptibilities of the dissolved salts.

% salt in the glass	χ obs $\times 10^6$ of the glass	χ calc (of dissolved salt from additivity formula) $\chi^M \times 10^6$		χ(of pure salt) $\times 10^6$	$\chi_M \times 10^6$
$NaCl—Na_2B_4O_7$ system					
8.97	—0.6667	—1.937	—113.2*	—0.499	—29.17
14.85	—0.6573	—1.320	— 77.18		
15.22	—0.6965	—1.559	— 91.16		
16.84	—0,7276	—1.646	— 96.25		
17.22	—0 7580	—1 799	—105.2		
$Li_2SO_4—Na_2B_4O_7$ system					
7.02	—0.5846	—1.1541	—126.89	—0.38	—41.77
9.55	—0.6759	—1.9479	—214.15		
11.50	—0.7145	—2.0452	—224.84		
12.98	—0.7643	—2.2574	—248.18		
$Na_2SO_4—Na_2B_4O_7$ system					
8.68	—0 6195	—1 4389	—204.40	—0.337	—47.87
10.67	—0.6591	—1.6428	—233.37		
13.43	—0 7292	—1.9384	—275.35		
15.62	—0.7752	—2.0372	—289 38		
17.36	—0.8455	—2.2922	—325.60		
17.71	—0 8563	—2.3186	—329.35		
$K_2SO_4—Na_2B_4O_7$ system					
5.46	—0.558	—0.8417	—146.68	—0.403	—70.22
8 64	—0.581	—0.9976	—173.83		
11.14	—0.6c7	—1.1286	—196,67		
15.38	—0.654	—1.2724	—221.72		
18.42	—0.758	—1.7165	—299.1		

DISCUSSION

It appears from the results that the values of the susceptibility of the dissolved salts in glass as calculated from the addivitity formula are very much greater than those of the pure crystals. The variation is much greater than is usually found with aqueous solutions. In a subsequent communication this point will be elucidated.

The gm.-atomic susceptibility of a dia-magnetic mono-nuclear system is given according to the simple Langevin theory by

$$\chi = -\frac{e^2}{6mc^2} \cdot \sum n\bar{r}^2 \qquad \ldots \quad (4)$$

where n is the number of electrons in the system,

$\sum \bar{r}^2$ is the summation of the squares of the radii of the projected orbits in a plane perpendicular to the magnetic field, e is the electronic charge, m, the mass and c, the velocity of the electron.

It is apparent, therefore, that an increase in the dia-magnetic susceptibility points to increased electronic orbits or what comes to the same thing, in the case under investigation, an enlargement of the lattice of the dissolved crystals. That the lattice exists in such systems has been proved by workers in this laboratory (Majumdar and Palit,1942, 1945, and Majumdar, Banerjee and Banerjee, 1945.)

With NaCl the molecular susceptibility is found to vary between -77 to -105×10^{-6} corresponding to a concentration range between 14.85 – 17.22%, the value for the pure salt being only -28.63×10^{-6}. The former values are abnormally large and cannot be accounted for by any compound formation as the cations in the dissolved salt and the solvent medium are the same. Mole-refraction measurements of these salts dissolved in the same glass (Majumdar and Banerjee, *loc. cit.*) throws an interesting light. The values of R_{NaCl} in such systems are remarkably small indicating a strong deformation of the dissolved salt. The slope of the mole-refraction—concentration curve, however is not so steep as that of the susceptibility—concentration curve for this salt. And this is true for the other salts investigated in this paper. A strong deformation would naturally mean a closer packing of the lattice with consequent *decrease* of the spacing, the susceptibility measurements on the other hand point clearly to an *increase* of the spacing. This point was sought to be cleared by X-ray diffraction experiments. The preliminary measurements of Majumdar and Palit (*loc. cit.*) seemed to support such a conclusion and this is also supported by theoretical considerations regarding the forces operating within an electro-static lattice. The purely electro-static (Coulomb) forces between the charges as well as the short-distance repulsive forces will be decreased by the introduction of a medium of higher dielectric constant as borax glass and a new equilibrium will be set up in which the spacing will be higher than in vacuum or in air. But subsequent work (*cf.* Majumdar, Banerjee and Banerjee, *loc. cit.*) did not reveal any appreciable change in the spacings of the dissolved salts.

In the case of the sulphates a very large increase of the susceptibilities is noticeable in every case. For Li_2SO_4, the molecular susceptibility increases

from—126.9 to—248.2 $\times 10^{-6}$ for concentration range between 7.02—12.98%, whereas the value for the pure crystal is only -41.7×10^{-6}. For Na_2SO_4 the increase is from -204.4 to -329.35×10^{-6} within the concentration range 8.68—17.17%, the value for the pure crystal being only -47.8×10^{-6}, and for K_2SO_4, the values lie between -146.68 and -299.1×10^{-6} for the concentration range 5.46—18.42%, the corresponding value for the pure salt being only -70.22×10^{-6}. Such abnormal increase in the values cannot be explained merely by cationic exchange, which, however, is not possible in the two of the four cases, namely NaCl-$Na_2B_4O_7$ and Na_2SO_4-$Na_2B_4O_7$ systems.

It is wellknown, however, that a small difference does exist between the values of susceptibilities of salts in dilute aqueous solution and in the solid state, as would be seen from the following table,

TABLE III

Gm.-molecular susceptibilities of salts

$-\chi_M \times 10^6$.

	Solid	Aqueous solution
NaCl ...	30.1	30.8
KCl ...	39.1	39.6
$CaCl_2$ ...	54.45	55.6

The increase, which in no case is more than a few percent, can be easily explained as due to the removal of the mutual polarisation of the outer electron shells of the ions in aqueous solution, which would naturally increase the average value of $\bar{r}^2$ within the meaning of equation (4). One would, therefore, expect to find a still smaller value of χ_M, as the deformation of the crystal in the glass is still greater. The results of magnetic susceptibility determination of salts dissolved in glass therefore run counter to those of mole-refraction and X-ray diffraction experiments.

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